

Photolysis of Formamides and Acetamides Studied by Electron Spin Resonance^{1a}

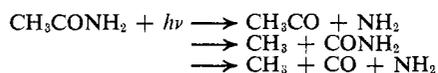
S. R. Bosco, Alexander Cirillo,^{1b} and Richard B. Timmons

Contribution from the Chemistry Department, The Catholic University of America, Washington, D. C. Received December 20, 1968

Abstract: The primary free-radical producing step in the photolysis of formamide is shown to be the formation of H atoms and CONH₂ radicals. Photolysis of acetamide produces CH₃ and CONH₂. Substitution of a methyl group on the nitrogen atom in these compounds does not change the primary step in that C–H and C–C bond scission is observed for N-methylformamide and N-methylacetamide, respectively. The free radicals produced at –196° were identified from their esr absorption spectra. The use of deuterium-labeled samples and generation of free radicals by OH radical attack on the parent molecules were used to help identify the free radicals produced in the photochemical decompositions.

The use of esr spectroscopy to identify the free radicals produced in photochemical decompositions has been employed in a number of reactions. Recently Volman and coworkers have used this technique in elucidating the photochemistry of aliphatic amines,^{2a} as well as with some sulfur-containing compounds.^{2b} This method was shown to be very useful in solving problems associated with the photodecomposition of nitro and nitroso compounds.³ In this type of work, photolyses are carried out in rigid matrices, usually at –196°. Under these conditions the resulting esr absorption lines are quite broad; however, the resolution has been sufficiently good to provide unequivocal evidence for the primary steps in the above-mentioned photodecompositions. In this paper we report the results of our esr study of the free radicals produced in the photolysis of formamide, acetamide, and their N-methyl derivatives.

The photolysis of acetamide has been the subject of several studies. In aqueous solution, the photolysis was suggested to lead to CH₃CO and NH₂ formation, followed by subsequent decomposition of the acetyl radical.⁴ However, in dioxane or hexane solution the primary decomposition has been reported to be nonfree radical in nature but occurs *via* direct formation of CH₃NH₂ and CO.⁵ Gas-phase photolysis of acetamide has been shown to produce CH₃, CO, and NH₂.⁶ However, at the temperatures required for the gas-phase work any initially formed radicals such as CONH₂ and CH₃CO would undergo unimolecular decomposition, and it was not possible to distinguish among the following primary steps.



In addition to these reactions, direct molecular formation of CH₃CN and H₂O was reported.⁶

(1) (a) This research was supported by the Public Health Service, Grant No. GM-14110; (b) National Science Foundation Undergraduate Research Participant, Summer 1968.

(2) (a) S. G. Hadley and D. H. Volman, *J. Amer. Chem. Soc.*, **89**, 1053 (1967); (b) D. H. Volman, J. Wolstenholme, and S. G. Hadley, *J. Phys. Chem.*, **71**, 1798 (1967).

(3) B. H. J. Bielski and R. B. Timmons, *ibid.*, **68**, 347 (1964).

(4) D. H. Volman, *J. Amer. Chem. Soc.*, **63**, 2000 (1941).

(5) G. H. Booth and R. G. W. Norrish, *J. Chem. Soc.*, 188 (1952).

(6) B. C. Spall and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A239**, 1 (1957).

In view of the above results, we felt that definitive information on the photochemistry of acetamide might be obtained from the esr absorptions of free radicals produced in these reactions. Acetamide is a particularly interesting molecule to study because at the wavelengths employed ($\lambda < 2500 \text{ \AA}$) a number of reactions are energetically feasible including C–C, C–N, N–H, and C–H bond breakage.

In addition, almost no information is available on the photochemistry of formamide or the N-methyl derivatives of formamide or acetamide. Accordingly, the study was extended to include these molecules. We feel that our results provide direct evidence of the primary steps leading to free-radical production in the photolysis of these compounds.

Experimental Section

The amides employed were Fisher spectroscopic grade quality. Aqueous samples of the amides were prepared of various concentrations ranging from 5 to 30% by weight of the amides. A change in amide concentration caused no observable changes in the esr spectra of the free radicals produced by the photolysis. Dissolved oxygen was removed from the samples by a repeated freezing and pumping technique. Deuterated samples were prepared by simply allowing the amide hydrogens to exchange in D₂O solution for a few hours, then pumping off the D₂O–H₂O mixture.⁷ This process was repeated three times, resulting in amides which had exchanged essentially all their N–H hydrogens. This was shown to be true *via* nmr analysis. No exchange of the hydrogen bonded to carbon could be observed in any of these compounds in agreement with previous reports.⁸

Samples were frozen to –196° in "Suprasil" quartz sample tubes and irradiated at that temperature. Irradiation of the samples was carried out using a General Electric UA-2 medium pressure mercury lamp. In view of the absorption coefficients of the amides and the experimental technique used, it is estimated that most of the effective radiation was in the wavelength range from 2000 to 2500 Å. After photolysis, the sample was transferred to the esr cavity which was precooled to approximately –185°. Absorptions were recorded using a Varian V-4503 esr spectrometer plus variable-temperature accessory. In many cases, samples were annealed at higher temperatures (up to –100°) and variations in the spectra were noted.

In some experiments free radicals were produced *via* OH radical attack on the parent compounds. In these experiments 2% H₂O₂ solutions of the amides were photolyzed with a Pyrex window employed to filter out short-wavelength radiation. Warming of the samples after photolysis produced spectra which we can attribute to OH radical attack on the amides. With the Pyrex window in

(7) L. H. Piette, J. D. Ray, and R. A. Ogg, *J. Mol. Spectry.*, **2**, 66, (1958).

(8) R. Livingston and H. Zeldes, *J. Chem. Phys.*, **47**, 4173 (1967).

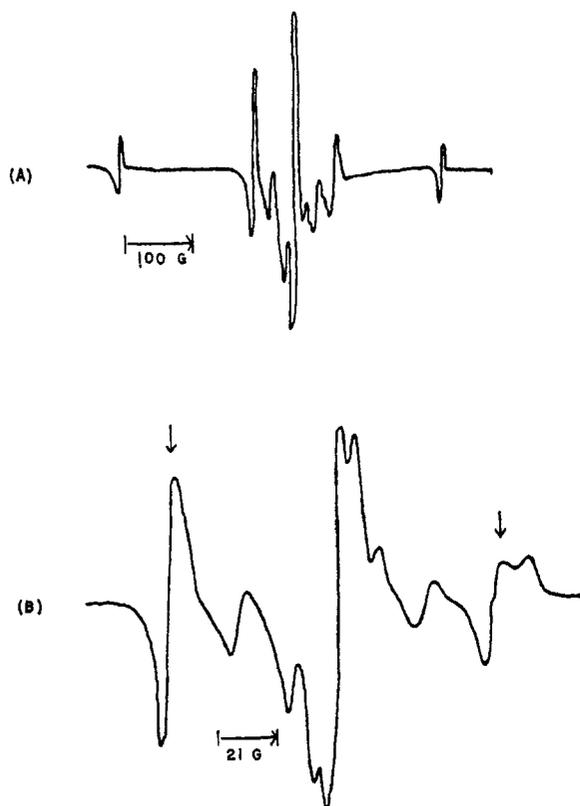


Figure 1. ESR spectra of HCONH_2 irradiated at -196° for 1 hr: (A) part of a 1000-G scan showing H atom absorptions; (B) 250-G scan of the central portion, the arrows indicating the CHO radical.

place, photolysis of the amide solution alone produced no observable free-radical absorption spectra.

In general, photolysis times were limited to 3 min or less in order to avoid complications from secondary photolysis of free radicals initially produced. However, in some cases, particularly for formamide, much longer times were employed as noted in the next section.

Results and Discussion

Formamide. The esr spectra obtained in the photolysis of formamide in a water matrix is shown in Figure 1A for a 1000-G scan, and the central portion of this spectrum is shown in higher resolution with a 250-G scan in Figure 1B. Both spectra were recorded at -180° . In Figure 1A, the absorption lines separated by 510 G can be attributed only to H-atom absorption. In Figure 1B, the central portion of the esr signal from formamide photolysis reveals a number of interesting factors. The strong signals labeled with the arrows on either end of the spectrum are undoubtedly from the CHO radical. The coupling constant for these lines is 135 G in agreement with that reported by a number of workers.⁹ In addition the spectrum is identical with that of the CHO radical reported by Sullivan and Koski¹⁰ including the asymmetry of the high-field line.

In our work we have found that the formyl radical signals are strongly time dependent, increasing in intensity with increasing time of photolysis much faster than the central region of the spectrum. In Figure 1B, it is seen that after 1 hr of photolysis, the formyl radical signals are very prominent. In contrast to this, Figure

(9) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1661 (1962).

(10) P. J. Sullivan and W. S. Koski, *J. Amer. Chem. Soc.*, **85**, 384 (1963).

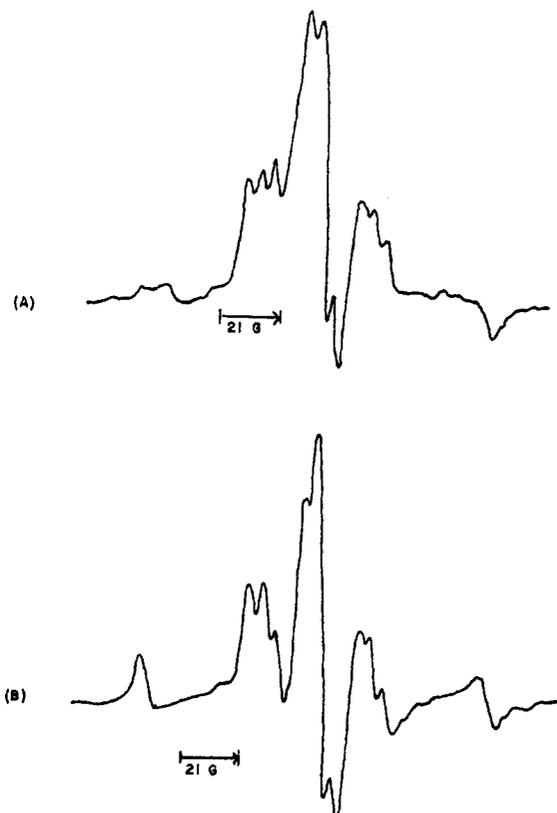


Figure 2. ESR spectra of HCOND_2 irradiated at -196° : (A) spectrum obtained after 3-min photolysis; (B) spectrum after 8-min photolysis.

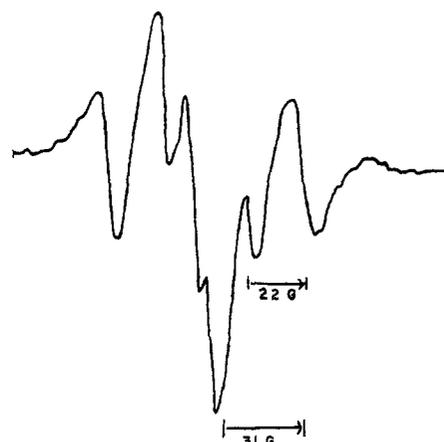


Figure 3. ESR spectrum of the free radical produced by OH radical attack on HCONH_2 .

2 demonstrates that in the photolysis of HCOND_2 the HCO absorption after 3 min of photolysis is very weak, increasing significantly after a total photolysis time of 8 min, while the central absorption remains relatively constant. From these observations we conclude that the HCO radical is being produced by secondary processes and not *via* direct photolysis of formamide.

In order to establish the identity of the central spectra, it was necessary to compare the esr absorption spectra obtained from HCONH_2 with that from HCOND_2 (Figure 2) as well as the free radical obtained from the attack of OH radicals on HCONH_2 (Figure 3). In this analysis we rely heavily on the work of Livingston and Zeldes⁸ who obtained high-resolution spectra in solu-

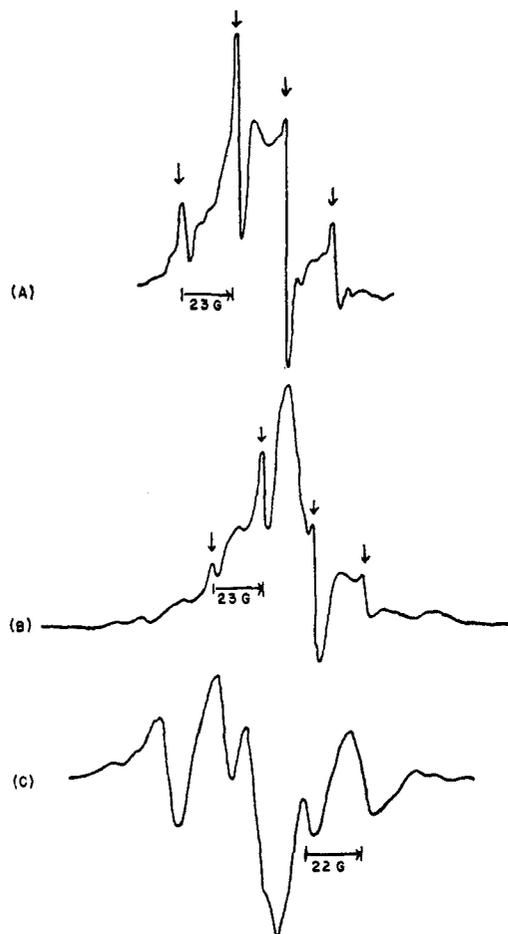


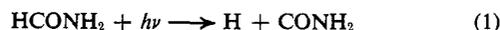
Figure 4. ESR spectra obtained in the photolysis of acetamide irradiated at -196° : (A) spectrum recorded at -180° , (B) spectrum recorded at -140° , (C) spectrum recorded after the sample was warmed to -120° for several minutes and then cooled to -180° . Spectrum was recorded at -180° . In spectra A and B, arrows indicate the positions of CH_3 absorption.

tion of the free radicals produced by photolysis of formamide mixed with H_2O_2 or CH_3COCH_3 . In both of these cases, they observed esr absorptions which could be attributed to the CONH_2 radical. Unusual spin parameters were observed for this radical in that it was shown that the two hydrogens are not equivalent. The coupling constants observed for this radical at 32° were $a^{\text{N}} = 21.69$ G, $a_1^{\text{H}} = 1.27$ G, and $a_2^{\text{H}} = 30.41$ G. The inequivalence of the two hydrogens and their vastly different coupling constants was reasonably explained in terms of the formation of a "non- π " radical having hindered rotation about the C-N bond.

The spectrum we obtain in the photolysis of aqueous mixtures of formamide and H_2O_2 is shown in Figure 3. Quite clearly the spectrum consists of six lines, all of approximately equal intensity. It has been shown⁸ that the OH radical produced by the decomposition of H_2O_2 will preferentially abstract an H atom from the CHO group of formamide to form CONH_2 . The coupling constant between the lines shown of 22 and 31 G are in excellent agreement with that shown by Livingston and Zeldes for CONH_2 . In the solid matrix the absorption lines are too broad to be able to resolve the hyperfine structure from the weakly coupled hydrogen and thus we observe only six lines. This assignment is further confirmed in the photolysis of HCOND_2

where it is seen that the six lines have been replaced by three sets of triplets (Figure 2). The coupling constants of 5 G between each line in the triplet and 21 G between central lines of adjacent triplets is in excellent agreement with the values for the COND_2 radical observed by Livingston and Zeldes.⁸

In view of the observation of H-atom signals, the CONH_2 and COND_2 spectra and the much stronger time dependence of the CHO signal relative to the CONH_2 absorption, we conclude that the only major free-radical producing step in this photolysis is



We feel that the HCO we observe might arise from a disproportionation reaction between H atoms and CONH_2 , or possibly by H-atom addition to CO formed by the subsequent photolysis of CONH_2 . It has been demonstrated previously that at low temperatures H atoms do indeed add to CO to form HCO.⁹ If either of these processes are occurring, then we should also observe absorption by NH_2 radicals. Unfortunately these signals would be masked somewhat by the CONH_2 radical. In addition, the NH_2 radical concentration would probably be a good deal less than that of the CHO radical in view of its greater reactivity and perhaps greater mobility in the solid matrix.

Acetamide. The results of the photolysis of acetamide are shown in Figure 4. The spectra consist of a quartet of lines in an intensity ratio of 1:3:3:1 plus a remaining six-line spectrum. The decrease in intensity of these lines with increasing temperature is also shown in Figure 4. The quartet disappears rapidly with increasing temperature whereas the remaining lines show relatively little change up to temperatures of -120° . The coupling constants of 23 G for the quartet, their intensity ratio, and their rapid disappearance at higher temperatures are consistent with the behavior of CH_3 radicals. The spectrum remaining after the CH_3 radicals have disappeared is identical with the CONH_2 radical as shown in Figure 3. On the basis of this result we feel the primary step in the photolysis of acetamide is



This assignment was confirmed by the photolysis of CH_3COND_2 . The spectrum of the remaining radical obtained after annealing out the CH_3 is identical with that obtained from the photolysis of HCOND_2 .

We feel that any photolysis to produce CH_3CO and NH_2 must represent a relatively insignificant primary step. The formation of CH_3CO would have produced a quartet of lines, 17 G apart and in an intensity ratio of 1:3:3:1.¹¹ We do not observe any such lines and thus conclude that reaction 2 adequately represents the primary step in acetamide photolysis. In this sense we do not agree with the work of Booth and Norrish who concluded that acetamide photolysis proceeds *via* an entirely nonfree radical process.

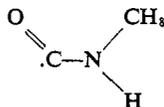
N-Methyl Derivatives. A typical spectrum obtained from N-methylformamide is shown in Figure 5A. In addition H-atom signals were again observed. Identical spectra were obtained in the case of N-methylacetamide, Figure 5B, with the exception that the spec-

(11) J. R. Morton and W. E. Falconer, *Nature*, **197**, 1103 (1963).

tra showed the presence of CH_3 radicals and the absence of H atoms. The photolysis of the deuterated N-methylformamide or N-methylacetamide produced no change in the esr spectra. On the basis of these observations we feel that the primary steps in the photolysis of these substituted compounds are comparable to those obtained in the photolysis of formamide and acetamide, namely



In this way we can account for the similarity of the spectra shown in Figure 5. Both the nmr spectra of N-methylformamide and N-methylacetamide reveal the presence of only one isomer, believed to be the isomer with the N-H *trans* to the C=O group.⁷ Thus we believe that the esr signal shown in Figure 5 is caused by the radical



where free rotation about the C-N bond is not observed. However, it is impossible to assign any coupling constants for the various nuclei as the resolution is not sufficiently good under our experimental conditions. In addition from the work of Livingston and Zeldes⁸ with comparable radicals, it would appear likely that the C-H hydrogens are not equivalent, and thus one needs much better resolution than can be obtained in a solid matrix to make any definitive assignments.

Conclusions

We feel that this esr study provides unequivocal evidence that the main free-radical producing step in the photolysis of formamide and N-methylformamide is scission of the C-H bonds. Contrary to some previous reports, the photolysis of acetamide and N-methylacetamide is shown to produce free radicals, in both cases decomposition taking place at the C-C bond.

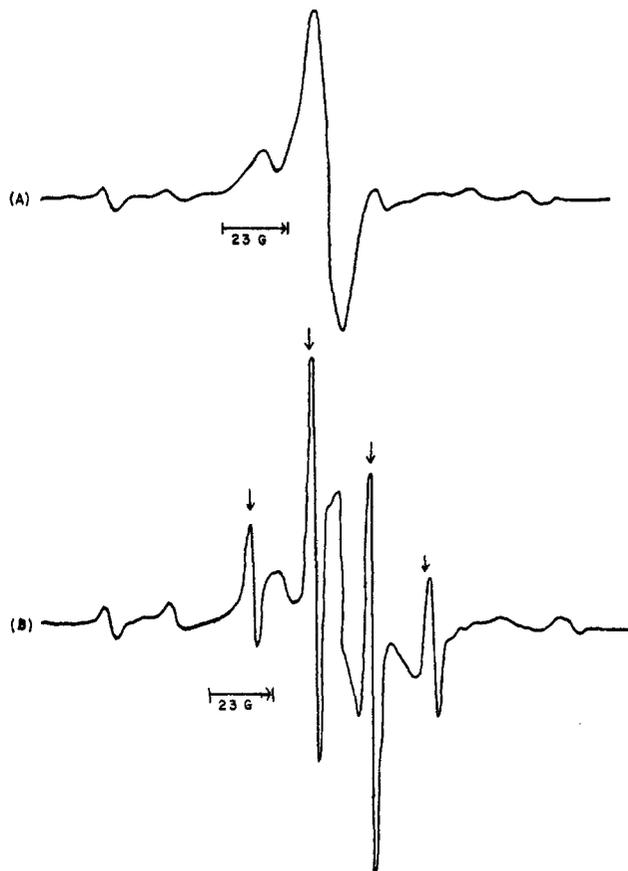


Figure 5. Esr spectra obtained in the photolysis of N-methyl derivatives of formamide and acetamide: (A) N-methylformamide, (B) N-methylacetamide. In spectrum B, the arrows indicate the positions of CH_3 absorption.

From our results we conclude that these reactions are the only major free-radical producing reactions. However, we must emphasize that these free-radical producing steps were observed at -196° . The primary mechanism might be different in the gas phase or in liquids at much higher temperatures.